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Abstract:
Tooth discoloration varies in etiology, appearance, localization, severity, and adhesion to tooth structures. It can be defined as being extrinsic or intrinsic on the basis of localization and etiology. This review article will help clinicians improve their understanding of the composition, mechanism of tooth bleaching, different types of bleaching and factors influencing tooth bleaching.

Keywords: Bleaching discolored teeth, esthetics.

INTRODUCTION
Aesthetics of the teeth is of great importance to patients, including tooth colour. The colour of the teeth is influenced by a combination of their intrinsic colour and the presence of any extrinsic stains that may form on the tooth surface. Intrinsic tooth colour is associated with the light scattering and adsorption properties of the enamel and dentine, with the properties of dentine playing a major role in determining the overall tooth colour.1,2 Extrinsic stains tend to form in areas of the teeth that are less accessible to tooth brushing and the abrasive action of a toothpaste and is often promoted by smoking, dietary intake of tannin-rich foods (e.g. red wine) and the use of certain cationic agents such as chlorhexidine, or metal salts such as tin and iron.2

Tooth colour can be improved by a number of methods and approaches including whitening toothpastes, professional cleaning by scaling and polishing to remove stain and tartar, internal bleaching of non-vital teeth, external bleaching of vital teeth, microabrasion of enamel with abrasives and acid, placement of crowns and veneers.1,2

Types of stains/discolorations
Discolorations may be extrinsic or intrinsic:
Extrinsic stains
Extrinsic stains usually result from the accumulation of chromatogenic substances on the external tooth surface. Extrinsic color changes may occur due to poor oral hygiene, ingestion of chromatogenic food and drinks, and tobacco use. These stains are localized mainly in the pellicle and are either generated by the reaction between sugars and amino acids or acquired from the retention of exogenous chromophores in the pellicle. The reaction between sugars and amino acids is called the “Millard reaction” or the “non-enzymatic browning reaction,” and includes chemical rearrangements and reactions between sugars and amino acids. The chemical analysis of stains caused by chromatogenic food demonstrates the presence of furfurals and furfuraldehyde derivatives due to this reaction. In addition, the retention of exogenous chromophores in the pellicle occurs when salivary proteins are selectively attached to the enamel surface through calcium bridges; consequently, a pellicle will form. At the early stage of staining, chromogens interact with the pellicle via hydrogen bridges. Most extrinsic tooth stains can be removed by routine prophylactic procedures. With time, these stains will darken and become more persistent, but they are still highly responsive to bleaching.3,4

Intrinsic stains
Intrinsic stains are usually caused by deeper internal stains or enamel defects. They are caused by aging, ingestion of chromogenetic food and drinks, tobacco usage, enamel microcracks, tetracycline medication, excessive fluoride ingestion, severe jaundice in infancy, porphyria, dental caries, restorations, and the thinning of the enamel layer. Aging is a common cause of discoloration. Over time, the underlying dentin tends to darken due to the formation of secondary dentin, which is darker and more opaque than the original dentin, and when the overlying enamel becomes thinner. This combination often results in darker teeth. Excessive fluoride in drinking water, greater than 1–2 ppm, can cause metabolic alteration in ameloblasts, resulting in a defective matrix and improper calcification of teeth. Discoloration from drug ingestion may occur either before or after the tooth is fully formed. Tetracycline is incorporated into the dentin during tooth calcification, probably through chelation with calcium, forming tetracycline orthophosphate, which causes discoloration. Moreover, intrinsic stains are also associated with inherited conditions (e.g., amelogenesis imperfecta and dentinogenesis imperfecta). Blood penetrating the dental tubules and metals released from dental restorative materials also cause stains. Intrinsic stains cannot be removed by regular prophylactic procedures. However, they can be reduced by bleaching with agents penetrating enamel and dentin to oxidize the chromogens. Tooth stains caused by aging, genetics, smoking, or coffee are the fastest to respond to bleaching: Yellowish aging stains respond quickly to bleaching in most cases, whereas blue–gray tetracycline stains are the slowest to respond to bleaching, while teeth with brown fluorescence are moderately responsive.6,9,10,11, 12

(a) **Thickening agents:** Carbopol (carboxypolymethylene) is the most commonly used thickening agent in bleaching materials. Its concentration is usually between 0.5% and 1.5%. This high-molecular-weight polyacrylic acid polymer offers two main advantages. First, it increases the viscosity of the bleaching materials, which allows for better retention of the bleaching gel in the tray. Second, it increases the active oxygen-releasing time of the bleaching material by up to 4 times.11, 12

(b) **Carrier:** Glycerin and propylene glycol are the most commonly used carriers in commercial bleaching agents. The carrier can maintain moisture and help dissolve other ingredients.11, 12

(c) **Surfactant and pigment dispersant:** Gels with surfactant or pigment dispersants may be more effective than those without them. The surfactant acts as a surface-wetting agent which permits the active bleaching ingredient to diffuse. Moreover, a pigment dispersant keeps pigments in suspension.11, 12

(d) **Preservative:** Methyl, propylparaben, and sodium benzoate are commonly used as preservative substances. They have the ability to prevent bacterial growth in bleaching materials. In addition, these agents can accelerate the breakdown of hydrogen peroxide by releasing transitional metals such as iron, copper, and magnesium.11, 12

(e) **Flavoring:** Flavorings are substances used to improve the taste and the consumer acceptance of bleaching products. Examples include peppermint, spearmint, wintergreen, sassafras, anise, and a sweetener such as saccharin.11, 12

**Mechanism of tooth bleaching**
The mechanism of bleaching by hydrogen peroxide is not well understood. In-office and home bleaching gels contain hydrogen peroxide or its precursor, carbamide peroxide, as the active ingredient in concentrations ranging from 3% to 40% of hydrogen peroxide equivalent. Hydrogen peroxide bleaching generally proceeds via the perhydroxyl anion (HO2 _). Other conditions can give rise to free radical formation, for example, by

**Composition of commercial bleaching agents**
Current bleaching agents contain both active and inactive ingredients. The active ingredients include hydrogen peroxide or carbamide peroxide compounds. However, the major inactive ingredients may include thickening agents, carrier, surfactant, and pigment dispersant, preservative, and flavoring.6,9,10,11, 12
homolytic cleavage of either an O–H bond or the O–O bond in hydrogen peroxide to give $\text{H}_2 + _\text{OOH}$ and $2\_\text{OH}$ (hydroxyl radical), respectively. Under photochemical reactions initiated by light or lasers, the formation of hydroxyl radicals from hydrogen peroxide has been shown to increase. Hydrogen peroxide is an oxidizing agent that, as it diffuses into the tooth, dissociates to produce unstable free radicals which are hydroxyl radicals ($\text{HO}_2$), perhydroxyl radicals ($\text{HOO}_2$), perhydroxyl anions ($\text{HOO}_2^-$), and superoxide anions ($\text{OO}_2^-$), which will attack organic pigmented molecules in the spaces between the inorganic salts in tooth enamel by attacking double bonds of chromophore molecules within tooth tissues. The change in double-bond conjugation results in smaller, less heavily pigmented constituents, and there will be a shift in the absorption spectrum of chromophore molecules; thus, bleaching of tooth tissues occurs.9,10

In the case of tetracycline-stained teeth, the cause of discoloration is derived from photo-oxidation of tetracycline molecules available within the tooth structures. The bleaching mechanism in this case takes place by chemical degradation of the unsaturated quinone-type structures found in tetracycline, leading to fewer colored molecules. Vital bleaching via a long-term night guard can sometimes improve the color of tetracycline-stained teeth.13,14

More recently, amorphous calcium phosphate (ACP) has been added to some of the tooth whitening products, to reduce sensitivity, reduce the demineralization of enamel through a remineralization process after whitening treatments, and add a lustrous shine to teeth.9,10 A study proved that the bleaching treatments promoted increased sound enamel demineralization, while the addition of Ca ions or ACP did not prevent/reverse the effects caused by the bleaching treatment in both conditions of the enamel. Early artificial caries induced by pH cycling model were not affected by the bleaching treatment, regardless of the type of bleaching agent.8,10

**TYPES OF DENTAL BLEACHING PROCEDURES**

**VITAL TOOTH BLEACHING**

There are three fundamental approaches for bleaching vital teeth: in-office or power bleaching, at-home or dentist supervised night-guard bleaching, and bleaching with over-the-counter (OTC) products.13,14

**In-office bleaching**

It utilizes a high concentration of tooth-whitening agents (25–40% hydrogen peroxide). Here, the dentist has complete control throughout the procedure and has the ability to stop it when the desired shade/effect is achieved. In this procedure, the whitening gel is applied to the teeth after protection of the soft tissues by rubber dam or alternatives, and the peroxide will further be activated (or not) by heat or light for around one hour in the dental office.14 Different types of curing lights including; halogen curing lights, Plasma arc lamp, Xe–halogen light (Luma Arch), Diode lasers (both 830 and 980 nm wavelength diode lasers), or Metal halide (Zoom) light can be used to activate the bleaching gel or accelerate the whitening effect. The in-office treatment can result in significant whitening after only one treatment, but many more may be needed to achieve an optimum result.14

**Fig 1: In office bleaching**
Fig 2: Curing Light

At-home or Dentist-supervised Night-guard bleaching
It basically involves the use of a low concentration of whitening agent (10–20% carbamide peroxide, which equals 3.5–6.5% hydrogen peroxide). In general, it is recommended that the 10% carbamide peroxide be used 8 h per day, and the 15–20% carbamide peroxide 3–4 h per day. This treatment is carried out by the patients themselves, but it should be supervised by dentists during recall visits. The bleaching gel is applied to the teeth through a custom-fabricated mouth guard worn at night for at least 2 weeks. This technique has been used for many decades and is probably the most widely used. The at-home technique offers many advantages: self administration by the patient, less chair-side time, high degree of safety, fewer adverse effects, and low cost. Despite the fact that patients are able to bleach at their own pace, this at-home bleaching technique, with its various concentrations of bleaching materials and regimens, has become the gold standard by which other techniques are judged. However, it is by no means without disadvantages, since active patient compliance is mandatory and the technique suffers from high dropout rates. In addition, color change is dependent on diligence of use, and the results are sometimes less than ideal, since some patients do not remember to wear the trays every day. In contrast, excessive use by overzealous patients is also possible, which frequently causes thermal sensitivity, reported to be as high as 67%. A 35% concentration of hydrogen peroxide is recommended by some clinicians for in-office dental bleaching, followed by at-home bleaching with gels containing 10%, 15%, or 20% carbamide peroxide. Bailey and Swift (1992) showed that higher-concentration bleaching agents can produce more peroxide radicals for bleaching, resulting in a faster whitening process. However, this rapid process of bleaching may increase the side-effects of tooth sensitivity, gingival irritation, throat irritation, and nausea.

Over-the-counter (OTC) bleaching
These products are composed of a low concentration of whitening agent (3–6% hydrogen peroxide) and are self-applied to the teeth via gum shields, strips, or paint-on product formats. They are also available as whitening dentifrices, prefabricated trays, whitening strips, and toothpastes. They should be applied twice per day for up to 2 weeks. OTC products are considered to be the fastest growing sector of the dental market. However, these bleaching agents may be of highly questionable safety, because some are not regulated by the Food and Drug Administration.

Fig 3 : Bleaching kit

NON-VITAL TOOTH BLEACHING
There are numerous non-vital bleaching techniques used today, for example, walking
bleach and modified walking bleach, non-vital power bleaching, and inside/outside bleaching.\textsuperscript{29}

**Walking bleach technique**  
It involves sealing a mixture of sodium perborate with water into the pulp chamber of the affected tooth, a procedure that is repeated at intervals until the desired bleaching result is achieved.\textsuperscript{29}

**Modified Bleaching Technique**  
This technique is modified with a combination of 30\% hydrogen peroxide and sodium perborate sealed into the pulp chamber for one week; this is known as modified walking bleach.\textsuperscript{27}

**Internal non-vital power bleaching**  
Hydrogen peroxide gel (30–35\%) is placed in the pulp chamber and activated either by light or heat, and the temperature is usually between 50 and 60 °C maintained for five minutes before the tooth is allowed to cool for a further 5 min. Then, the gel is removed, the tooth is dried, and the ‘walking bleach technique’ is used between visits until the tooth is reviewed 2 weeks later to assess if further treatment is needed.\textsuperscript{26}

**Inside/outside bleaching**  
This technique is a combination of internal bleaching of non-vital teeth with the home bleaching technique.\textsuperscript{28}

The majority of contemporary tooth whitening studies involve the use of either hydrogen peroxide or carbamide peroxide. This latter material is an adduct of urea and hydrogen peroxide which on contact with water breaks down to urea and hydrogen peroxide. In general, the efficacy of hydrogen peroxide containing products are approximately the same when compared with carbamide peroxide containing products with equivalent or similar hydrogen peroxide content and delivered using similar format and formulations, either tested in vitro\textsuperscript{11} or in vivo. For example, Nathoo et al. demonstrated in a clinical study that a once a day application of either a 25\% carbamide peroxide gel or a 8.7\% hydrogen peroxide gel both gave a statistically significant tooth shade lightening after 2 weeks use compared to baseline, but found no statistically significant differences between products. Similarly, other potential vital tooth bleaching systems have been outlined in the literature with limited supporting evidence for their efficacy. These include sodium perborate, peroxymonosulphate, peroxide plus metal catalysts and oxireductase enzymes. The long-term acceptability and relative efficacy of these alternative tooth bleaching systems requires significant further research.\textsuperscript{28,29}

**Concentration and time**  
Two of the key factors in determining overall tooth whitening efficacy from peroxide containing products are the concentration of the peroxide and duration of application. For example, Sulieman et al. compared the in vitro tooth bleaching efficacy of gels containing 5–35\% hydrogen peroxide and found that the higher the concentration, the lower the number of gel applications required to produce uniform bleaching.\textsuperscript{14} Similar results were found by Leonard et al. who compared the in vitro tooth bleaching efficacy of 5\%, 10\% and 16\% carbamide peroxide gels and found the whitening was initially faster for the 16\% and 10\% than the 5\% concentration. However, the efficacy of the 5\% approached the higher concentrations when the treatment time was extended. In a clinical study using custom made bleaching trays, Kihn et al. showed that a 15\% carbamide peroxide gel
gave significantly more tooth whitening than a 10% carbamide gel after 2 weeks use. This result was confirmed in another clinical study reported by Matis et al. However, in this latter study, by extending treatment time to 6 weeks, the differences in tooth lightness were no longer of statistical significance. The initial faster rate of bleaching for higher concentrations of carbamide peroxide has also been observed when bleaching tetracycline stained teeth in vivo over a 6 months period. In this case, the most rapid whitening occurred in the first month with 20% carbamide peroxide compared to 15% and 10% carbamide peroxide. In addition, clinical studies with hydrogen peroxide strip based products have shown similar concentration and time effects for tooth whitening efficacy.

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Heat and light
The rate of chemical reactions can be increased by increasing the temperature, where a 10°C rise can double the rate of reaction. The use of high-intensity light, for raising the temperature of the hydrogen peroxide and accelerating the rate of chemical bleaching of teeth was reported in 1918 by Abbot. Contemporary approaches and literature has focussed on accelerating peroxide bleaching with simultaneous illumination of the anterior teeth with various sources having a range of wavelengths and spectral power, for examples, halogen curing lights, plasma arc lamps, lasers and light-emitting diodes. For some light sources, significant increases in pulpal temperatures have been measured using in vitro models during tooth bleaching. The light source can activate peroxide to accelerate the chemical redox reactions of the bleaching process. In addition, it has been speculated that the light source can energise the tooth stain to aid the overall acceleration of the bleaching process. Some products that are used in light activated bleaching procedures contain ingredients that claim to aid the energy transfer from the light to the peroxide gel and are often coloured materials, for examples, carotene and manganese sulphate.

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Concluding remarks
The importance of tooth whitening for patients and consumers has seen a dramatic rise in the number of tooth whitening products and procedures. Concomitantly, there has been a rapid increase of published in vivo and in vitro tooth whitening studies. Indeed, it is clearly evident that there is an extensive literature describing their efficacy and safety. However, some of this literature is conflicting, and these topics warrant further careful evaluation as they were outside the scope of the current review. A number of approaches to measuring tooth colour changes following tooth whitening exist, each with their own advantages and disadvantages, and this topic is likely to be an area commanding further research in the future. With the continued interest in tooth whitening amongst basic and clinical researchers, the further mechanistic understanding and optimisation of the factors controlling the tooth whitening process will continue to expand. This will give further improvements to the tooth whitening products and procedures, and give significant benefits to the field of aesthetic dentistry. This will ultimately lead to the enhancement of patient compliance and satisfaction with the whitening outcome.

REFERENCES

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